Belagbildung auf Wärmetauscherflächen: Kann man sie verhindern?

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Fouling on Heat Exchanger Surfaces: Can it be Prevented?

Braunschweig, 08.02.2002*

Abstract

A measure to reduce fouling is an extension of the induction time by a defined modification of interfacial interactions between heat transfer surface and crystalline deposit. Because these interactions are caused by molecular and mechanical forces, two approaches for fouling mitigation have been developed:

1. Modification of the energy related properties of the heat transfer surface.
2. Modification of the geometry related properties of the heat transfer surface.

Introduction

The formation of fouling layers on heat transfer surfaces is a severe problem for industry. Due to insulation these crystalline deposits contribute to the overall heat transfer coefficient deteriorating the performance of heat exchangers considerably [1].

The fouling process can be divided into two periods, induction and fouling period. Within the induction period the formation of stable nuclei at the heat transfer surface and the crystal growth takes place. In the succeeding fouling period an increase of the fouling resistance

$$R_f = \frac{1}{k_f} - \frac{1}{k_o} \tag{1}$$

due to scale formation can be measured, with k_f overall heat transfer coefficient for the fouled and k_o for the clean heat transfer surface.

Both induction and fouling period consist of a deposition and a removal process described by the deposition mass rate $\dot{m}_d$ and the removal mass rate $\dot{m}_r$, respectively. The deposition mechanism of the induction period is a function of the nucleation rate, whereas the removal mechanism is mainly influenced by the adhesion between crystals and heat transfer surface as described in Fig. 1.

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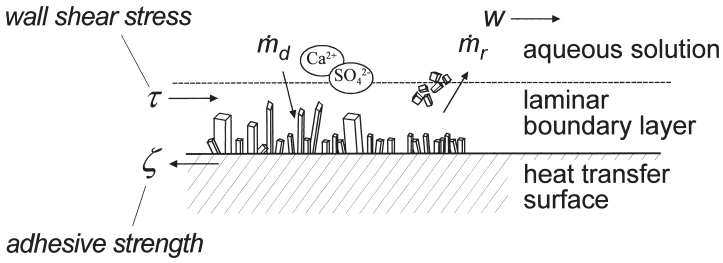

Fig. 1: Deposition and removal during the induction period

Modern anti-fouling strategies are based on approaches increasing the duration of the induction period and, hence, decreasing the adhesive strength of the crystals. In order to relate physical properties of the interface crystal/heat transfer surface to adhesion the interfacial interactions have to be analyzed.

Fig. 2 gives an overview of interactions playing a decisive role in adhesion. Oliveira [2] gave a detailed description of the relevant interactions.

Mechanical interactions can influence adhesion because single crystals will attach preferably at specific profile elements of the surface contour.

The description of molecular interactions are based on the assumption that dispersive and polar Lifshitz-van der Waals forces are predominant during the induction period. According to van Oss [3] Lewis acid-base interactions in salt solutions can cause anomalies in the theoretical interpretation of interfacial interactions refering to Lifshitz-van der Waals forces. For some materials repulsive electron donor-electron acceptor interactions based on the Lewis acid-base theory can develop. In addition, the commonly repulsive double layer forces due to the tendency of particular materials to aquire an electrical charge when immersed in polar media are important. Other molecular forces, e.g. caused by Born repulsion, can be neglected.

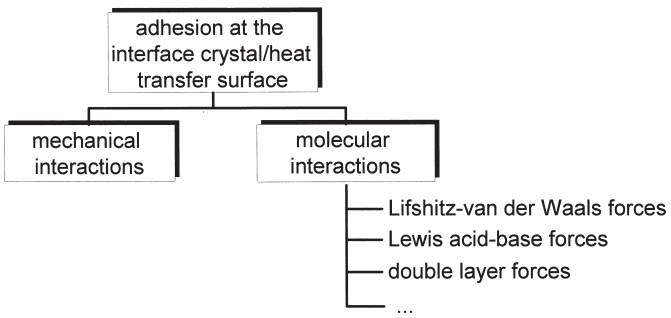

Fig. 2: Interfacial interactions influencing adhesion

Experiments

A better understanding of the key factors influencing the induction period may help to design more efficient heat exchangers. A mobile test unit including a plate heat exchanger has been built in order to validate fouling mitigation techniques which have been developed theoretically. A detailed description of the test unit has been given by Förster and Bohnet [4].

In order to evaluate the dependence of fouling behaviour on surface material during the induction period, the physical mechanisms taking place at the interface crystal/heat transfer surface have to be analyzed. An important parameter influencing molecular interactions is the interfacial free energy

$$\gamma_{ij} = \left(\frac{\partial G}{\partial A} \right)_{T,p} \tag{2}$$

defined as the total reversible work to create an interfacial area at the interface of the phases i and j. Here, G denotes the Gibbs free energy of the system, T the temperature and p the pressure. If the adjacent phase j is air or vacuum, γ_{ij} is also called "surface free energy" of phase i. In the following sections interfacial interactions are treated on the basis of an equilibrium of three phases in contact according to Fig. 3. A spherical droplet (phase 1) of a test liquid is resting on the heat transfer surface (phase 2) in a surrounding phase (phase 3). Here, the sign "~" is used to distinguish between interfacial energies referred to droplets and crystals.

Resolving the interfacial free energies given in Fig. 3 in horizontal direction leads to the Young equation:

$$\gamma_{23} = \gamma_{12} + \tilde{\gamma}_{13} \cdot \cos\theta_{12} \tag{3}$$

In order to calculate the surface free energy $\gamma_{12}$of the heat transfer surface, the suceeding procedure has to be carried out:

1. Determination of $\tilde{\gamma}_{13}$ which is the surface tension of the test liquid (pendant drop method or literature data).

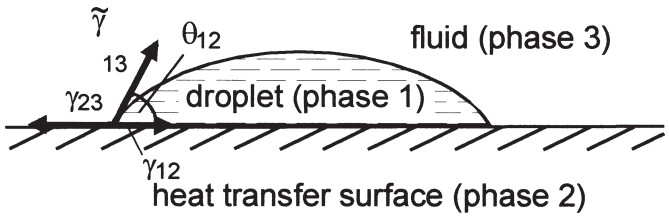

Fig. 3: Wetting equilibrium

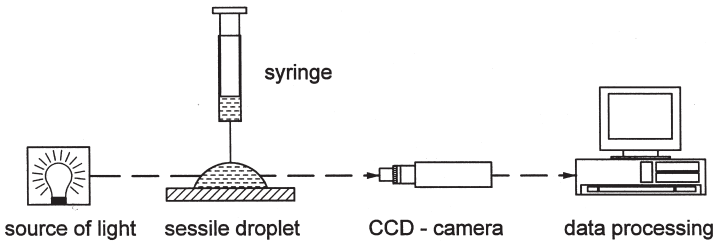

Fig. 4: DSA measurement device

2. Measuring the contact angle θ_{12} by DSA (drop shape analysis) as outlined in Fig. 4. Here, a droplet of a test liquid is placed upon the surface to be characterized. By means of a CCD camera and a data processing system the image of the liquid droplet is digitized. Afterwards, the contour of the droplet is analyzed with respect to the determination of θ_{12}which is the contact angle corresponding to the wetting equilibrium.

3. Substitution of the interfacial free energy between droplet and heat transfer surface γ_{12} in Eq. (3) using the geometric/harmonic mean or the Lewis acid-base approach according to Tab. 1: The restrictions of Egs. (4-6) and the corresponding assumptions are discussed in detail by Förster and Bohnet [5].

4. Calculation of γ_{23}. DSA-measurements with at least two (geometric/ harmonic mean approach) or three test liquids (Lewis acid-base approach) enables to solve the system of equations.

In order to evaluate the influence of mechanical interactions at the interface crystal/heat transfer surface on the induction period of precipitation fouling, a measurement station for

Table 1: Calculation of γ_{12}

geometric mean method:

$$\gamma_{12} = \gamma_{13}^{LW} + \gamma_{23}^{LW} - 2\left(\sqrt{\gamma_{13}^{dis}\gamma_{23}^{dis}} + \sqrt{\gamma_{13}^{pol}\gamma_{23}^{pol}}\right) \quad (4)$$

harmonic mean method:

$$\gamma_{12} = \gamma_{13}^{LW} + \gamma_{23}^{LW} - 4\left(\frac{\gamma_{13}^{dis}\gamma_{23}^{dis}}{\gamma_{13}^{dis} + \gamma_{23}^{dis}} + \frac{\gamma_{13}^{pol}\gamma_{23}^{pol}}{\gamma_{13}^{pol} + \gamma_{23}^{pol}}\right) \quad (5)$$

Lewis acid-base approach:

$$\gamma_{12} = \gamma_{12}^{LW} + \gamma_{12}^{AB} = \left(\sqrt{\gamma_{13}^{LW}} - \sqrt{\gamma_{23}^{LW}}\right)^2 + 2\left(\sqrt{\gamma_{13}^{+}\gamma_{13}^{-}} + \sqrt{\gamma_{23}^{+}\gamma_{23}^{-}} - \sqrt{\gamma_{13}^{+}\gamma_{23}^{-}} - \sqrt{\gamma_{13}^{-}\gamma_{23}^{+}}\right) \quad (6)$$

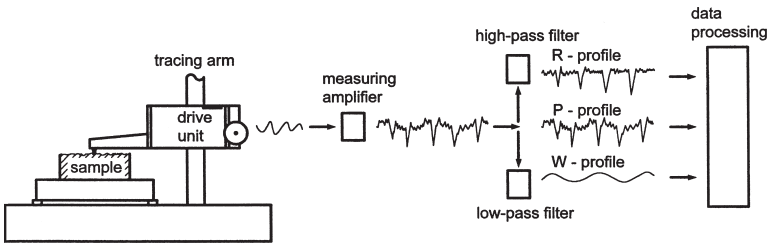

Fig. 5: Topography measuring unit

roughness, micro contours and topography has been used. The most important component is the high-precision drive unit featuring a motor-driven height adjustment for lowering and lifting the pick-up and for setting it to zero automatically. For the evaluation of surface contour the R-profile (roughness profile) is deployed which results by filtering the original P-profile (primary profile).

Influence of Surface energy on induction period

Fig. 6 shows the influence of surface material on both induction period and gradient of the fouling curve. The deployment of new surface materials such as DLC-coatings (diamond like carbon) proved to be a strategy to increase the duration of the induction period significantly.

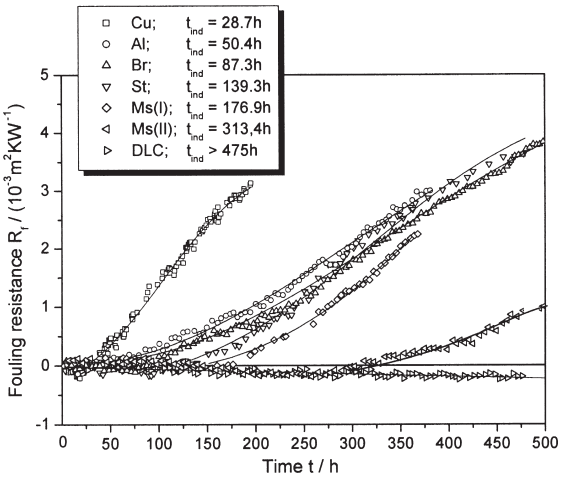

Fig. 6: Influence of surface material on fouling

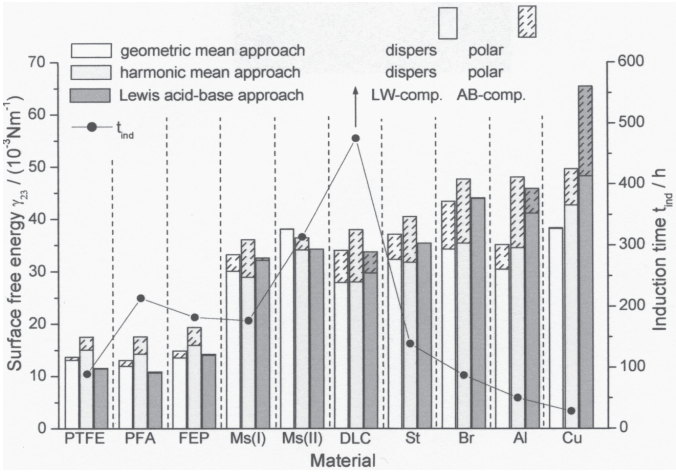

Fig. 7 Surface energy and induction time

In Fig. 7 the results of wetting experiments on metallic and polymeric heat transfer surfaces are summarized. In addition, the measured induction time t_{ind} is given. For the DLC coating, t_{ind} has to be extrapolated in the direction of the ordinate because no increase in fouling resistance versus time could be detected after $475h$. The physical properties of the test liquids needed for the calculation of γ_{23} are taken from Förster, Augustin and Bohnet [6].

The comparision of surface energy data with induction time yields no correlation between surface energy and fouling behaviour. Thus, the choice of surface material with respect to least fouling occurence cannot be based on surface properties of the heat transfer surface, only. In order to find the optimal surface material the adjacent crystalline deposit has to be taken into account since the latter phase also influences molecular interaction at the interface crystal/heat transfer surface.

Interfacial defect model

An approach to combine the energy related characteristics of heat transfer surface and deposit is the interfacial defect model. According to Fig. 8 the principles of wetting equilibria are used to describe crystallization.

Since the same phases interact with each other, the unknown interfacial energy γ_{13} corresponding to crystallization may be replaced by the interfacial energy fouling layer/ heat transfer surface γ_{23} related to wetting experiments. The surface energies γ_{23} of both fouling layer (adhesive) and heat transfer surface (substrate) are accessible using the DSA measurement technique. Hence, the interfacial free energy adhesive/substrate γ_{12} can be calculated by the geometric mean, harmonic mean or Lewis acid-base method as described

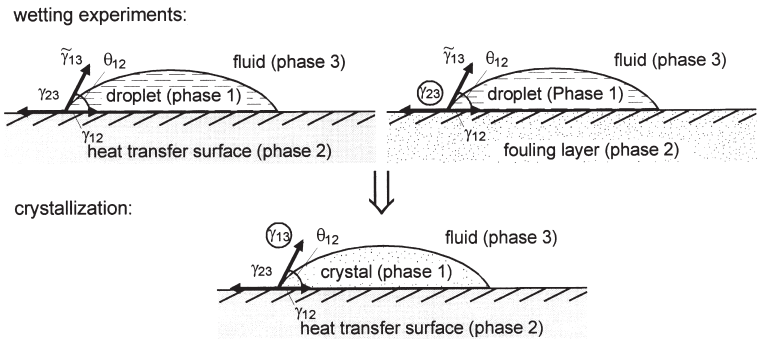

Fig. 8: Transferring the wetting model to describe crystallization during the induction period

by Förster and Bohnet, [5]. Using the Lewis acid-base method, the DSA on the adjacent side of a fouling layer yields

$$\gamma_{13}^{LW} = 46.17 mNm^{-1};\ \gamma_{13}^{AB} = 1.41 mNm^{-1},\ \gamma_{13}^{+} = 0.02 mNm^{-1};\ \gamma_{13}^{-} = 24.88 mNm^{-1};\ \gamma_{13} = 47.58 mNm^{-1}$$

γ_{13}^{LW} and γ_{13}^{AB} are the Lifshitz-van der Waals and acid-base components of the total interfacial energy γ_{13}. γ_{13}^{+} and γ_{13}^{-} denote the electron acceptor and donator components.

The interfacial defect model is based on the definition of the spreading coefficient.

$$\lambda_{12} = \gamma_{23} - \gamma_{13} - \gamma_{12} \tag{7}$$

Increasing values of are λ_{12} accompanied by an improved wettability and, as a consequence, by an increase of the adhesive strength z due to less interfacial defects. The model is capable to relate wetting characteristics to the adhesive strength z as defined by Wu [7],

$$\zeta = C \cdot \left(1 - \frac{\lambda_{12}}{\gamma_{23}}\right)^{-1} \tag{8}$$

C refers to the mechanical properties of the system such as the Young's modulus. In Fig. 9 t_{ind} is presented as a function of λ_{12}

The plot includes data for metallic and polymeric heat transfer surfaces. The interfacial defect model seems to be valid for metallic heat transfer surfaces whereas the deployment of polymeric surfaces materials leads to a significant deviation of the corresponding data points from the regression curve. This can be explained by the influence of surface topography on precipitation fouling.

In order to mitigate heat exchanger fouling, the choice of surface material should lead to high negative values of λ_{12}.

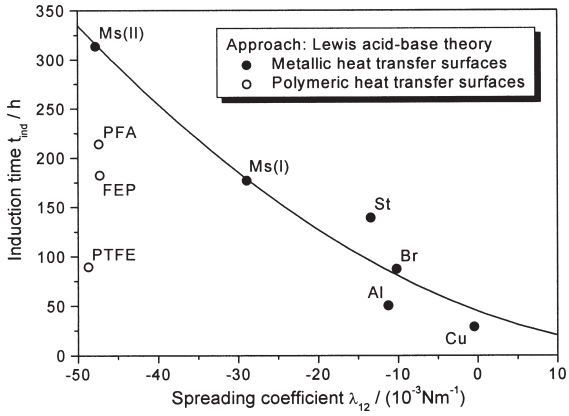

Fig. 9: Induction time versus spreading coefficient

Influence of Surface topography on induction period

In Fig. 10 the surface contour of stainless steel is compared with the surface contour of PTFE. Due to the width of profile elements of the PTFE surface the probabilty that crystals will attach increases. Besides wetting theories to describe adhesion, for polymer coatings the contribution of mechanical interactions caused by surface texture has to be considered.

Aa first approach to describe the influence of surface topography on the induction period, the well known mean roughness depth R_Z is deployed. R_Z is the arithmetic mean value of the single roughness depths of five consecutive sampling lengths derived by one roughness measurement (Fig. 11):

$$R_Z = \frac{1}{5} \cdot \sum_{i=1}^{5} Z_i \tag{9}$$

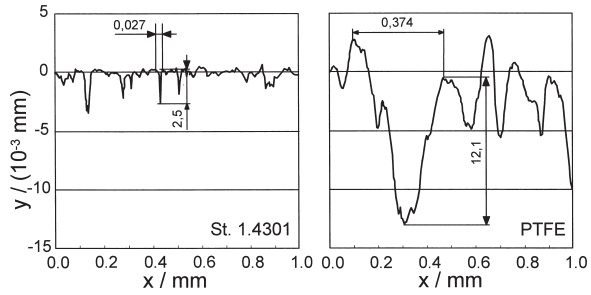

Fig. 10 Surface contours of a metallic and polymeric heat transfer surface

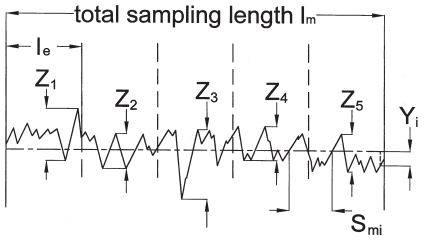

Fig. 11: Evaluation of the R-profile

Fouling experiments with various surface topographies have been carried out to examine the dependence of fouling behaviour on R_Z. The results according to Fig. 12 emphasize the importance of surface roughness for precipitation fouling.

Common surface texture parameters such as the the mean roughness depth R_Z give only a poor description of the influence of surface geometry on fouling (Fig. 13). By means of R_Z the surface contour is described in vertical direction only, though widths of profil elements can serve as regions for preferred nucleation.

R_{Sm} has been chosen for the evaluation of surface geometry in horizontal direction. R_{Sm} is defined as the arithmetic mean value of the widths of profile elements:

$$R_{Sm} = \frac{1}{n} \cdot \sum_{i=1}^{n} S_{mi} \tag{10}$$

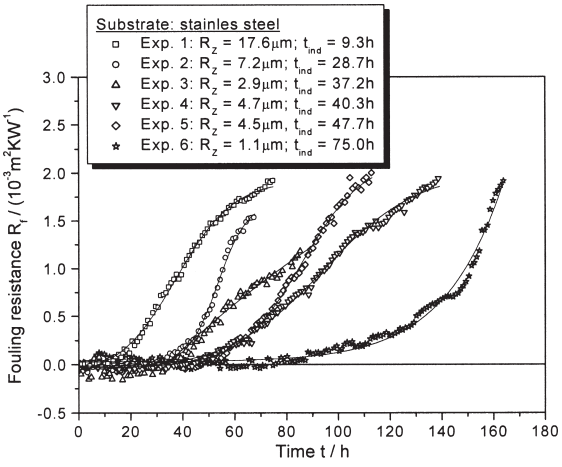

Fig. 12 Fouling resistance versus time as a function of surface roughness

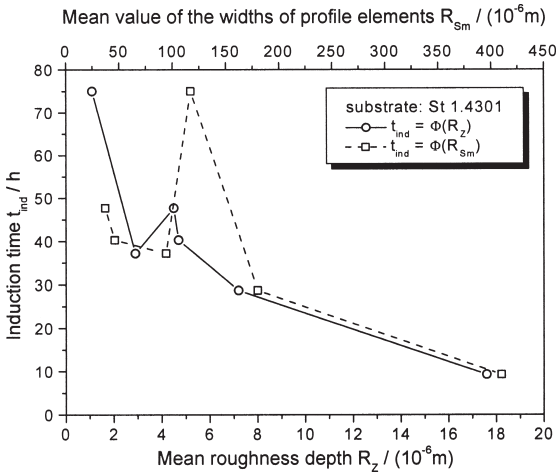

Fig. 13 Induction time as a function of single roughness parameters

According to Fig. 13, neither R_Z nor R_{Sm} correlates with t_{ind}. With respect to the interface model presented in Fig. 14 and various fouling as well as topographical experiments a new parameter for the describtion of the surface texture is proposed, which characterise both R_Z and R_{sm}:

$$K = R_z \cdot R_{sm} \tag{11}$$

Thus, a two-dimensional information of surface contour is received. Fig. 15 shows the dependence between t_{ind} and K for a stainless steel surface.

The electropolished steel substrate (experiment 6) is close to the optimum finish of an heat transfer surface. In order to mitigate heat exchanger fouling a small *K*-value has to be

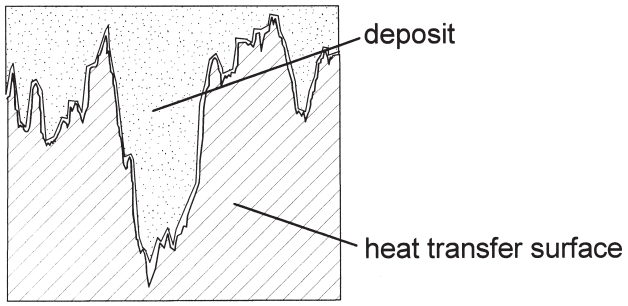

Fig. 14 Model of the interface between crystalline deposit and heat transfer surface

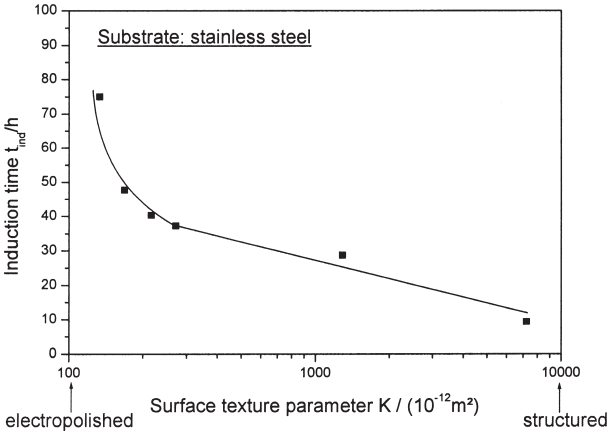

Fig. 15 Induction time versus surface texture parameter

realized. By means of Fig. 15 experiments with heat transfer surfaces having different surface energies and geometries can be related to a specific surface topography. In Fig. 16 the fouling experiments discussed so far are related to a surface texture parameter K, which describe technical roughness.

For metals and polymers the conclusion can be drawn that the Lewis acid-base approach is capable to desribe the relationship between wetting and crystallization characteristics.

The molecular interactions between a DLC coated surface and the fouling layer (λ_{12} = -16.9mNm^{-1}, $t_{ind} > 475h$) cannot be described by the Lewis acid-base theory because interfacial interactions such as electrostatic double layer forces are predominat.

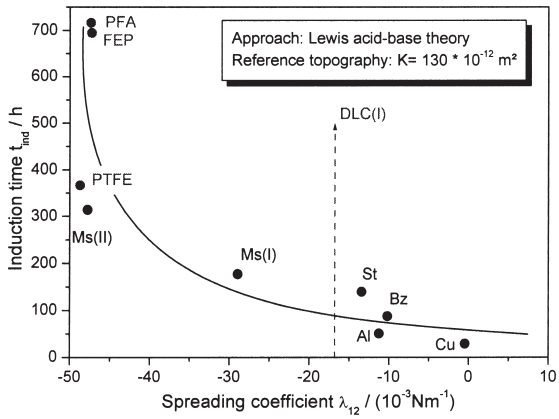

Fig. 16 Minimum induction time versus spreading coefficient

Conclusions and Prospect

For minimization heat exchanger fouling the interfacial defect model has been analyzed with respect to its ability to identify the optimal choice of surface material. Dispersive and polar Lifshitz-van der Waals forces as well as Lewis acid-base interactions have been considered by the introduction of a spreading coefficient. A two-dimensional surface texture parameter has been defined in order to make allowance for mechanical interactions due to surface topography. The spreading coefficient and the surface texture parameter allows an optimum selection of heat transfer surfaces.

Future research should contribute to the improvement of the description of interfacial interactions. Then, also double layer forces should be implemented.

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Nomenclature

C	constant, Nm^{-2}
G	Gibbs free energy, J
h	enthalpy, J
K	surface texture parameter, m^{-2}
$\dot{m}$	mass flow rate per unit area, $kgm^{-2}s^{-1}$
p	pressure, Pa
R_f	fouling resistance, m^2KW^{-1}
R_{Sm}	mean value of the widths of profile elements, m
R_Z	mean roughness depth, m
T	temperature, K
t	time, h
w	flow velocity, ms^{-1}
γ_{ij}	interfacial free energy between two adjacent phases i and j, Nm^{-1}
λ_{12}	spreading coefficient of adhesive 1 on substrate 2, Nm^{-1}
θ	contact angle, *degree*
ζ	adhesive strength, Nm^{-2}

Subscript

AB	Lewis acid-base
d	deposition
dis	dispersive
ind	induction period
LW	Lifshitz - van der Waals
pol	polar
r	removal
1	adhesive phase
2	substrate phase
3	surrounding phase
50	median value
~	test liquid
+	electron acceptor
-	electron donor

Abbreviations

Al	aluminium
Br	bronze
Cu	copper
DLC	diamond like carbon
DSA	drop shape analysis
FEP	fluorinated ethylene propylene
PFA	perfluoroalkoxy copolymer
Ms	brass
PTFE	polytetrafluor ethylene
St	stainless steel

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